

## Graphical Abstract

### TiO<sub>2</sub> nanorods based self-supported electrode of 1T/2H MoS<sub>2</sub> nanosheets decorated by Ag nano-particles for efficient hydrogen evolution reaction

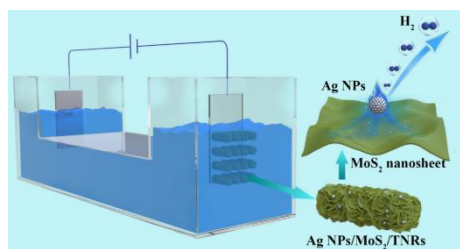
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An innovative strategy for preparation of electrocatalytic hydrogen evolution electrodes (Ag NPs/MoS<sub>2</sub>/TNRs) was proposed by organic acid-controlled hydrothermal method and electrodeposition. MoS<sub>2</sub> nanosheets with excellent hydrogen adsorption capacity transfer hydrogen to Ag NPs with weak hydrogen adsorption capacity through "hydrogen spillover", and induce hydrogen to combine into H<sub>2</sub> to achieve high hydrogen evolution catalytic activity.

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# TiO<sub>2</sub> nanorods based self-supported electrode of 1T/2H MoS<sub>2</sub> nanosheets decorated by Ag nano-particles for efficient hydrogen evolution reaction

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## ABSTRACT

Molybdenum disulfide (MoS<sub>2</sub>) has shown significant promise as an economic hydrogen evolution reaction (HER) catalyst for hydrogen generation, but its catalytic performance is still lower than noble metal-based catalysts. Herein, a silver nanoparticles (Ag NPs)-decorated 1T/2H phase layered MoS<sub>2</sub> electrocatalyst grown on titanium dioxide nanorod arrays (Ag NPs/1T(2H) MoS<sub>2</sub>/TNRs) was prepared through acid-tunable ammonium ion intercalation. Taking advantage of MoS<sub>2</sub> layered structure and crystal phase controllability, as-prepared Ag NPs/1T(2H) MoS<sub>2</sub>/TNRs exhibited ultrahigh HER activity. As-proposed strategy combines facile hydrogen desorption (Ag NPs) with efficient hydrogen adsorption (1T/2H MoS<sub>2</sub>) effectively circumvents the kinetic limitation of hydrogen desorption by 1T/2H MoS<sub>2</sub>. The as-prepared Ag NPs/1T(2H) MoS<sub>2</sub>/TNRs electrocatalyst exhibited excellent HER activity in 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> with low overpotential (118 mV vs reversible hydrogen electrode (RHE)) and small Tafel slope (38.61 mV/dec). The overpotential exhibits no obvious attenuation after 10 h of constant current flow. First-principles calculation demonstrates that as-prepared 1T/2H MoS<sub>2</sub> exhibit a large capacity to store protons. These protons can be subsequently transferred to Ag NPs, which significantly increases the hydrogen coverage on the surface of Ag NPs in HER process and thus change the rate-determining step of HER on Ag NPs from water dissociation to hydrogen recombination. This study provides a unique strategy to improve the catalytic activity and stability for MoS<sub>2</sub>-based electrocatalyst.

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Hydrogen is an extremely clean and renewable energy source, which is an ideal substitute of fossil fuels for environmental protection. Among the clean energy conversion methods, Hydrogen Evolution Reaction (HER) is one of the most promising methods for commercial application, which has attracted extensive attentions [1,2]. However, the main obstacle to hydrogen production from water electrolysis is a slow HER and large kinetic hindrance [3]. Platinum (Pt) has been widely studied as an excellent catalyst with extremely high electrical conductivity and excellent hydrogen adsorption and desorption for HER [4-7]. Unfortunately, the broad application of Pt-based catalysts are significantly limited by their high price and limited natural Pt proven reserves [8]. Thus, the development of Pt-free electrocatalysts with comparable performance, better stability and cost-effectiveness preparation process is imminent.

Researchers have recently investigated many low-cost and high-performance catalysts, mainly including transition metal dichalcogenides (TMDCs) [9-11], metal carbides [12], metal nitrides [13] and metal phosphides [14]. Among these candidates, molybdenum disulfide (MoS<sub>2</sub>) has attracted a lot of attention due to its two-dimensional layered structure and abundant catalytic active sites. Due to differences in the structure of layers (1, 2 and 3) and crystals (hexagonal, trigonal and rhombohedral) in a single unit cell, MoS<sub>2</sub> has three natural or synthetic polymorphisms, namely 1-trigonal (1T), 2-hexagonal (2H), and 3-rhombohedral (3R). Unlike 2H-MoS<sub>2</sub> phase, the 1T-MoS<sub>2</sub> phase exhibits metallic properties, so it has a high conductivity facilitating its HER performance [15]. Metastable 1T-MoS<sub>2</sub> can only be obtained under harsh synthetic strategies such as alkali metal intercalation-exfoliation [16,17], doping [18], mechanical strain [19], and electron beam irradiation [20]. However, the yields of the above methods are low, which severely limits the application of 1T-MoS<sub>2</sub>. It is a great challenge to obtain high-purity 1T-MoS<sub>2</sub> by a facile method. To address this issue, an acid regulation strategy is employed to efficiently induce phase transition from 2H-MoS<sub>2</sub> to 1T-MoS<sub>2</sub> for enhancing its HER performance [8,21]. To improve the conductivity of MoS<sub>2</sub>, the most widely used approach is coating conductive carbon on MoS<sub>2</sub> or loading MoS<sub>2</sub> on conductive carriers to reduce the charge transfer resistance in the electrochemical process [22,23]. Although the high 1T phase MoS<sub>2</sub>

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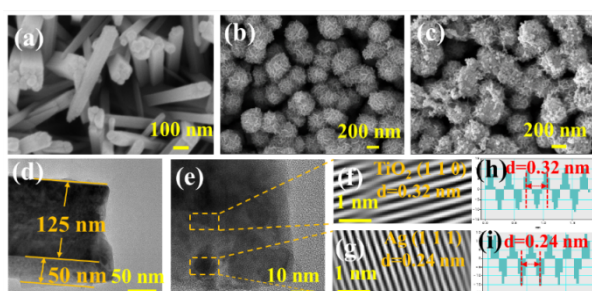
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catalyst synthesized by the above method improved the HER activity, its stability and surface charge transfer and internal resistance still have great challenges [24,25]. Therefore, it is necessary to develop a new type of MoS<sub>2</sub>-based catalyst with a facile growth approach but, high HER performance and stability.

Herein, a novel flower rod-like catalyst stacked by nanosheet MoS<sub>2</sub> was synthesized by hydrothermal grow MoS<sub>2</sub> on the surface of TiO<sub>2</sub> nanorods (TNRs) (Fig. S1a). The organic acid plays a major role in modulating the conversion efficiency of MoS<sub>2</sub> from 2H phase to the 1T phase which promotes electron transfer. Meanwhile, the internal resistance of charge transfer can be reduced by electrodepositing of Ag NPs. The resulting electrocatalyst exhibited excellent HER activity in 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> with low overpotential (118 mV vs. RHE) and small Tafel slope (38.61 mV/dec). Furthermore, as-prepared Ag NPs/MoS<sub>2</sub>/TNRs shows robust cycle stability and there is negligible overpotential attenuation after 10 hours of constant current flow.

Fig. S1b and Eqs. S1 (Supporting information) show the simple hydrothermal synthesis steps of MoS<sub>2</sub> in H<sub>2</sub>O as solvent (H-MoS<sub>2</sub>) nanoparticles and MoS<sub>2</sub> nanosheets on TNRs. In this experiment, thiourea as both sulfur source and reductant was employed to promote the formation of molybdenum blue (MB) from Mo-O-Mo bond condensation of protonated Mo-O-Mo under the action of propionic acid. As shown in Fig. S2 (Supporting information), MB species have the typical absorption band around 600-1100 nm which is attributed to the intervalence charge transfer (IVCT) [26]. The maximum absorbance is reached at the propionic acid volume fraction of 58.3% fraction of volume (vol). Fig. S3 (Supporting information) is the fourier transform infrared spectrometer (FT-IR) spectrum of MB powder, Mo-O bonds with different coordination oxygens have different characteristic absorption bands in the range of 1000-500 cm<sup>-1</sup> [27]. The band at 1414 cm<sup>-1</sup> corresponds to the bending vibration of the N-H in ammonium ions (NH<sub>4</sub><sup>+</sup>), indicating the presence of NH<sub>4</sub><sup>+</sup> bound to MB through strong electrostatic interaction [28,29]. The result of X-ray photoelectron spectroscopy (XPS) spectrum of the Mo 3d in Fig. S4 (Supporting information) confirms the presence of reduced Mo (V) species in the MB powder. As shown in Fig. S5 (Supporting information), graph element mapping analysis reveals a uniform distribution of Mo, S, C and O elements, further validating the formation of polyoxometalates (POMs) [29]. These data demonstrate that MB was successfully obtained by adding thiourea to sodium molybdate in the mixture of propionic acid and water.

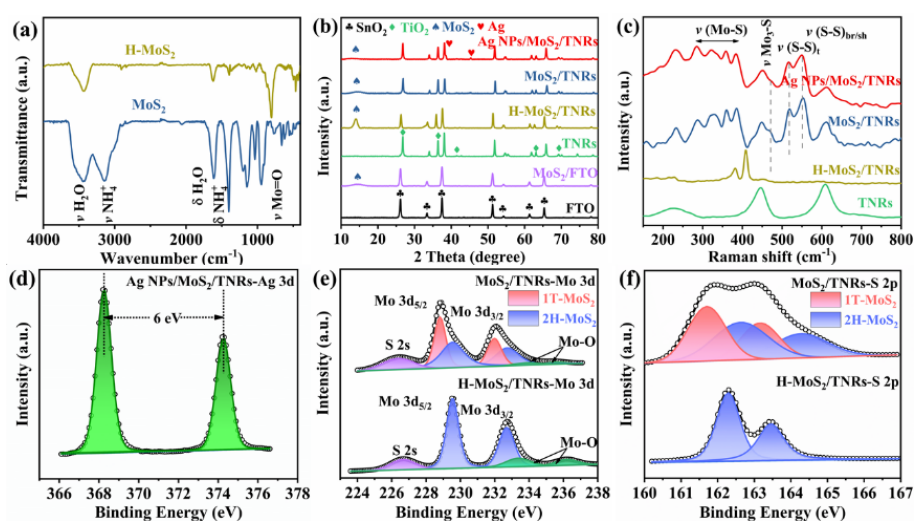
As shown in Fig. 1a, uniformly dense TNRs with an average diameter of 125 ± 5 nm are grown vertically on SnO<sub>2</sub> conductive glass doped with fluorine (FTO) surface. As shown in Fig. 1b, the MoS<sub>2</sub>/TNRs show a lamellae MoS<sub>2</sub> intercalated on the TNRs with a diameter of about 400 nm. As shown in Fig. 1c, the electrodeposition of Ag NPs is uniformly loaded on MoS<sub>2</sub>/TNRs. Meanwhile, Mo, S, Ti, O and Ag species are detectable and distributed uniformly over the entire sample (Figs. S6 and S7 in Supporting information). Comparing with MoS<sub>2</sub>/TNRs, the MoS<sub>2</sub>/FTO sample showed nanoflower morphology with a diameter of 1.2 μm, but the coverage of MoS<sub>2</sub> was also lower (Figs. S8a and b in Supporting information). MoS<sub>2</sub> on the H-MoS<sub>2</sub>/TNRs presents a rod-like stack on the surface of the TNRs, and the layered of MoS<sub>2</sub> has a larger electrochemically active area than the rodlike (Figs. S8c and d in Supporting information). As shown in Fig. 1d, the prepared Ag NPs/MoS<sub>2</sub>/TNRs electrodes are composed of TNR with a diameter of about 125 nm and MoS<sub>2</sub> (Ag NPs) with a thickness of 50 nm. The HRTEM (Figs. 1e, f and h) results further confirmed that the as-prepared TiO<sub>2</sub> nanorods possess the (110) plane for rutile TiO<sub>2</sub> [30]. The lattice fringe spacing of 0.24 nm (Figs. 1e, g and i) in the shell corresponds to the (111) plane of Ag NPs [31]. As shown in Fig. S9, MoS<sub>2</sub> was successfully loaded on TNRs, and Ag element is uniformly distributed on MoS<sub>2</sub>. SEM and TEM analysis confirm that the AgNO<sub>3</sub> precursor was successfully reduced to Ag NPs by electrodeposition. The close contact between Ag NPs and MoS<sub>2</sub> enables Ag NPs to efficiently transport electrons from Ag NPs to layered MoS<sub>2</sub>, which is crucial for the high HER performance of Ag NPs/MoS<sub>2</sub>/TNRs electrodes.



**Fig. 1.** Top view SEM images of (a) TNRs, (b) MoS<sub>2</sub>/TNRs and (c) Ag NPs/MoS<sub>2</sub>/TNRs. (d, e) high-resolution TEM (HRTEM) images of Ag NPs/MoS<sub>2</sub>/TNRs. The enlarged area denoted in (e) corresponding to the HRTEM images of (f) TiO<sub>2</sub> and (g) Ag, respectively. (h, i) Profile plots of the calibration for measuring the spacings of TiO<sub>2</sub> and Ag.

As shown in Fig. 2a, the peaks at 3133 and 1400 cm<sup>-1</sup> are due to the stretching and bending vibrations of the N-H bond, revealing the presence of intercalated NH<sub>4</sub><sup>+</sup> in the MoS<sub>2</sub>/TNRs [32]. The XPS spectra of N 1s of Fig. S10 (Supporting information) indicate the presence of intercalated NH<sub>4</sub><sup>+</sup>. The Intercalation of NH<sub>4</sub><sup>+</sup> as electron donors lead to the formation and stabilization of 1T-phase MoS<sub>2</sub> [33]. As shown in Fig. 2b, a broad molybdenum sulfide peak is observed only at 13.8° when an aqueous solution of propionic acid was used as the solvent for the hydrothermal preparation of MoS<sub>2</sub> [34]. The Ag NPs peaks in the X-ray diffraction (XRD) pattern of Ag NPs/MoS<sub>2</sub>/TNRs are detected at 2θ = 38.22° and 44.35° consistent with (111) and (200) plane (JCPDS card No. 04-0783) [35]. As shown

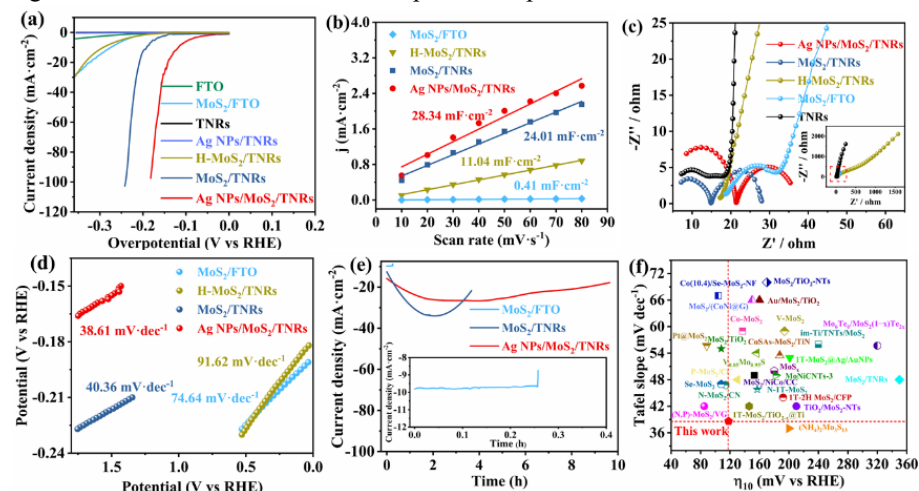
in Fig. 2c, at H-MoS<sub>2</sub>/TNRs, the characteristic Raman shifts at 408 and 452 cm<sup>-1</sup> expected for the E<sub>2g</sub><sup>1</sup> and A<sub>1g</sub> modes of 2H-MoS<sub>2</sub> are clearly observed [15,36]. At MoS<sub>2</sub>/TNRs, the vibration of bridging/shared disulfide ( $\nu(\text{S-S})_{\text{br/sh}}$ ) and terminal disulfide ( $\nu(\text{S-S})_t$ ) are found at 555 and 525 cm<sup>-1</sup>, respectively. Molybdenum sulfide bonds [37,38] are found at  $\nu(\text{Mo-S})$  of 382-284 cm<sup>-1</sup> whereas the  $\nu(\text{Mo}_3\text{-}\mu_3\text{S})$  vibration is detected at 450 cm<sup>-1</sup>. Raman vibration signatures of Ag NPs/MoS<sub>2</sub>/TNRs indicate that the disulfide ligands are not displaced after the electrodeposition of silver. As shown in Fig. S11, H-MoS<sub>2</sub>/TNRs, MoS<sub>2</sub>/TNRs and Ag NPs/MoS<sub>2</sub>/TNRs contain Ag (Ag NPs/MoS<sub>2</sub>/TNRs), S, Mo, C and O peaks without any impurity. As can be seen from the curve in Fig. S12 (Supporting information), the high-resolution Mo 3d spectrum of the MoS<sub>2</sub>/TNRs sample contains three spin-splitting doublets (Mo 3d<sub>5/2</sub> and Mo 3d<sub>3/2</sub>), where Mo 3d<sub>5/2</sub> peaks at  $\approx 228.8$  eV,  $\approx 229.5$  eV, and  $\approx 233.8$  eV. The feature at 228.8 eV and 229.5 eV is assignable to Mo<sup>4+</sup>, which is compatible with the binding energy of the 1T and 2H phase of MoS<sub>2</sub> [15,31]. Mo<sup>6+</sup> originates from the MoO<sub>3</sub> or MoS<sub>x</sub>O<sub>y</sub> regions in the electrodes (Figs. S11 and S13 in Supporting information) [39,40]. The high-resolution S 2p spectra in Fig. S14 further demonstrate the generation of 1T/2H MoS<sub>2</sub>. However, these peaks in the MoS<sub>2</sub>/TNRs and Ag NPs/MoS<sub>2</sub>/TNRs samples are red-shifted. This result proves the existence of electronic interaction between Ag NPs and MoS<sub>2</sub>. Furthermore, for the Ag 3d of Ag NPs/MoS<sub>2</sub>/TNRs (Fig. 2d), two peaks located at 368.3 eV and 374.3 eV prove the existence of metallic Ag, because the difference between the two peaks is 6.0 eV [41]. In Figs. 2e and f, H-MoS<sub>2</sub>/TNRs prepared with water as the only solvent have 2H-MoS<sub>2</sub> but no 1T phase MoS<sub>2</sub>. Therefore, XPS results along with electron microscopy, FT-IR, XRD, and Raman demonstrate the successful formation of the acid-controlled ammonium ion intercalated Ag NPs/MoS<sub>2</sub>/TNRs hybrid structure with high 1T phase MoS<sub>2</sub> and more active sites.



**Fig. 2.** (a) FT-IR spectra of H-MoS<sub>2</sub> and MoS<sub>2</sub> samples. (b) XRD patterns and (c) Raman spectra of Ag NPs/MoS<sub>2</sub>/TNRs and each component. (d) The high-resolution XPS spectra of Ag 3d from Ag NPs/MoS<sub>2</sub>/TNRs. The high-resolution XPS spectra of (e) Mo 3d and (f) S 2p from MoS<sub>2</sub>/TNRs and H-MoS<sub>2</sub>/TNRs.

The experimental results of Figs. S15 and S16 (Supporting information) showed that the overpotential was lowest at a propionic acid volume fraction of 58.3 vol% (Fig. S17 in Supporting information) and 3 mmol/L sodium molybdate and 15 mmol/L thiourea (48 mL solution). Fig. 3a shows that FTO, TNRs and Ag NPs/TNRs hardly exhibit the performance of electrocatalytic hydrogen evolution. Compared with H-MoS<sub>2</sub>/TNRs, MoS<sub>2</sub>/TNRs have higher electrocatalytic hydrogen evolution performance, which may be due to the high catalytic activity and high electrochemical active area of the 1T phase [15,18,39,42]. After silver electrodeposited, its electrocatalytic hydrogen evolution performance will be further improved, which may be due to electrocatalytic performance and high electrical conductivity of Ag [43]. The electrochemical double-layer capacitance ( $C_{dl}$ ) value of Ag NPs/MoS<sub>2</sub>/TNRs is determined to be 28.34 mF/cm<sup>2</sup>, which is 1.2, 2.6 and 69.1 times higher than that of MoS<sub>2</sub>/TNRs (24.01 mF/cm<sup>2</sup>), H-MoS<sub>2</sub>/TNRs (11.04 mF/cm<sup>2</sup>) and MoS<sub>2</sub>/FTO (0.14 mF/cm<sup>2</sup>), respectively (Fig. 3b and Fig. S18 in Supporting information). The maximum  $C_{dl}$  value of Ag NPs/MoS<sub>2</sub>/TNRs indicates the highest electrochemically active region with exposed active sites, which greatly enhances the HER performance [39]. The Nyquist curve (Fig. 3c) and equivalent circuit fitting (Fig. S19 and Table S1 in Supporting information) results show that MoS<sub>2</sub>/FTO and H-MoS<sub>2</sub>/TNRs have greater charge transfer resistance ( $R_{ct} = 4.83 \times 10^{11} \Omega$  and  $6.28 \times 10^4 \Omega$ ) compared with MoS<sub>2</sub>/TNRs. These results demonstrate that the crystal phase tuning and Ag NPs deposition can greatly facilitate charge transfer, thereby enhancing the reaction efficiency and promoting efficient electrical integration to reduce parasitic ohmic losses [44,45]. To get into the HER mechanism of these samples, we calculate the Tafel curves based on their linear sweep voltammetry (LSV) (Fig. 3d). The Tafel slope of Ag NPs/MoS<sub>2</sub>/TNRs is only 38.61 mV/dec, which is smaller than that of MoS<sub>2</sub>/TNRs (40.36 mV/dec), H-MoS<sub>2</sub>/TNRs (91.62 mV/dec) and MoS<sub>2</sub>/FTO (74.64 mV/dec), indicating that it is more consistent with the Heyrovsky-Tafel mechanism (Eq. S2 in Supporting information). Smaller Tafel slopes show faster HER reaction kinetics, resulting in efficient H<sub>2</sub> generation [42]. The stability of Ag NPs/MoS<sub>2</sub>/TNRs, MoS<sub>2</sub>/TNRs and MoS<sub>2</sub>/FTO are analysed by performing chronoamperometry test (Fig. 3e) at constant potentials ( $\eta_{10}$ ) of 120 mV, 210 mV and 280 mV vs. RHE, respectively. The presence of TNRs (MoS<sub>2</sub>/TNRs) and Ag NPs deposited on MoS<sub>2</sub> surface significantly enhance the stability. As shown in Fig. 3e and Fig. S20 (Supporting information), the polarization curves of Ag NPs/MoS<sub>2</sub>/TNRs after 10 h constant voltage test almost overlap, the overpotential at 10 mA/cm<sup>2</sup> changes from the initial 118 mV vs.

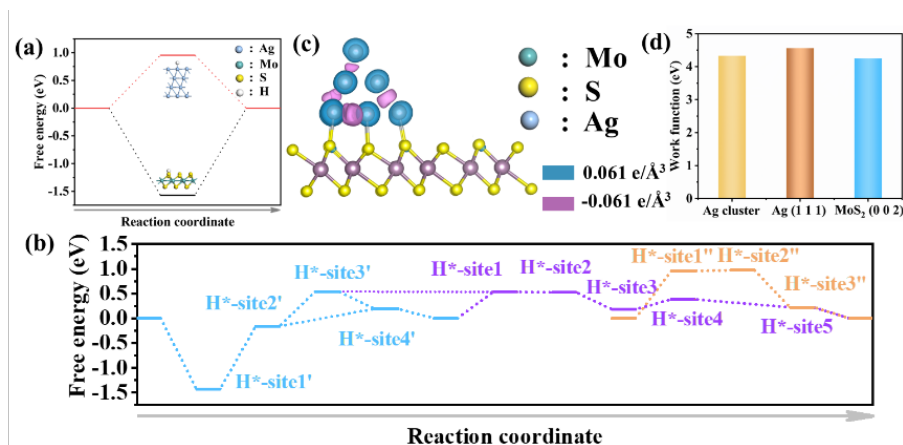
RHE to 123 mV vs. RHE, and the overpotential at 50 mA/cm<sup>2</sup> changes from the initial 163 mV vs. RHE to 169 mV vs. RHE. The above results indicate that TNRs provide good loading sites for MoS<sub>2</sub>, which has great advantages over FTO and the enhanced stability of 1T-MoS<sub>2</sub> is related to its substrate and surface electrodeposited Ag NPs. As summarised in Fig. 3f, the HER performance of the as-prepared Ag NPs/MoS<sub>2</sub>/TNRs is also better than previous reported Mo-based materials.



**Fig. 3.** (a) Polarization curves of electroplating silver in 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> solution with a scan rate of 5 mV/s. Capacitive currents with (b) various sweeping velocities, (c) Nyquist plot and (d) tafel plots of the electrodes. (e) Constant voltage response of MoS<sub>2</sub>/FTO, MoS<sub>2</sub>/TNRs and Ag NPs/MoS<sub>2</sub>/TNRs. (f) Comparison Tafel slope and  $\eta_{10}$  with other HER electrocatalysts reported recently. Values were plotted from references (Table S2 in Supporting information).

Hydrogen spillover, the migration of activated hydrogen atoms generated by the dissociation of di-hydrogen adsorbed on a metal surface onto a reducible metal oxide support, is a common phenomenon in heterogeneous catalysis [3]. To gain theoretical insights into whether hydrogen spillover can take place from MoS<sub>2</sub> to Ag NPs, density functional theory (DFT) calculation was carried out to determine the hydrogen transfer energy barriers. As shown in Fig. 4a, the adsorption of hydrogen is extremely weak on the surface of Ag (111), while the adsorption onto MoS<sub>2</sub> (002) is significantly enhanced, indicating that MoS<sub>2</sub> (002) is prone to hydrogen adsorption. As shown in Fig. 4b and Fig. S21 (Supporting information), the Gibbs free energy ( $\Delta G_{H^*}$ ) of adsorbed hydrogen in MoS<sub>2</sub> surface with the Ag absence (site 1') tends to be negative. The thermodynamic energy barrier of adsorbed hydrogen desorption to free hydrogen is 0.35 eV, indicating that hydrogen is difficult to desorb from site 2' to site 4'. At high hydrogen coverage, the  $\Delta G_{H^*}$  is 0.54 eV, and the thermodynamic energy barrier with the adsorbed hydrogen on the MoS<sub>2</sub> surface near Ag is 0.2 eV, indicating that the hydrogen transfer process from MoS<sub>2</sub> (site 3') to MoS<sub>2</sub> near Ag (site 1) is greatly promoted. Additionally, hydrogen adsorption is stronger on Ag NPs (site 4) which is combined to MoS<sub>2</sub> surface, which is more negative at site 4 than at site 1". Thus, adsorbed hydrogen can be spontaneously transferred to Ag from the MoS<sub>2</sub> adsorption site covered with high density hydrogen (from site 3' to site 5). To unravel the facilitated hydrogen transfer process on Ag NPs/MoS<sub>2</sub>, the charge density difference was calculated to explore the charge distribution at the interface. As shown in Fig. 4c, electron accumulation is observed below the surface layer of Ag. High density electrons are favorable to trap hydrogen atoms by interacting with unsaturated electrons in the H 1s orbital. As a result, hydrogen spillover from MoS<sub>2</sub> to Ag is thermodynamically and kinetically facilitated. To investigate charge transfer between Ag and MoS<sub>2</sub>, the work functions ( $\phi$ ) of Ag and MoS<sub>2</sub> were calculated. The work function of MoS<sub>2</sub> is determined to be 4.25 eV, smaller than that of Ag (4.33 eV), revealing electron transfer from MoS<sub>2</sub> to Ag (Fig. 4d and Fig. S22 in Supporting information). Combining with the above analyses, a reasonable explanation for hydrogen spillover from MoS<sub>2</sub> to Ag is given as follows: the difference in work function between Ag and MoS<sub>2</sub> leads to electron accumulation at the subsurface of Ag, which enhances the hydrogen adsorption on Ag surface and weakens the hydrogen adsorption on the MoS<sub>2</sub> surface, driving the desorption of hydrogen. As shown in Fig. S23 (Supporting information), it is difficult for adsorbed hydrogen on MoS<sub>2</sub> to evolve molecular hydrogen (Pathway 1). As a result, MoS<sub>2</sub> serves as an adsorbed hydrogen reservoir, which form hydrogen through Pathways 2-5.





**Fig. 4.** (a) Calculated free energy diagram for HER on MoS<sub>2</sub> and Ag. (b) Free energies of HER on MoS<sub>2</sub> and Ag were calculated for different hydrogen coverage and adsorption sites. (c) Electron density difference plot across the Ag-MoS<sub>2</sub> interface. Electron accumulation and depletion are indicated in blue and purple, respectively. (d) Work function calculations for various Ag and MoS<sub>2</sub>.

In conclusion, we proposed a layered phase 1T/2H Ag NPs/MoS<sub>2</sub>/TNRs as a high-performance and high-stability electrode for hydrogen evolution in acidic water electrolysis. The composite electrodes have excellent hydrogen evolution performance and low charge transfer resistance. The resulting composite electrodes exhibit good HER activity in 0.5 mol/L H<sub>2</sub>SO<sub>4</sub> solution with a low overpotential (118 mV vs. RHE) and a small Tafel slope (38.61 mV/dec). More importantly, after electrodeposition of Ag NPs, not only the performance of electrocatalytic hydrogen evolution is increased, but also its stability is significantly increased. These results suggest that Ag NPs, lamellar MoS<sub>2</sub>, and TNRs composites have a good synergy effect, which enables each component to play a unique role in efficient-performance of HER applications. DFT simulation and comprehensive characterisations suggest that the high HER catalytic activity of Ag NPs/MoS<sub>2</sub>/TNRs in acid possibly results from an unusual hydrogen spillover effect between multiple catalytic sites, whereby MoS<sub>2</sub> site captures proton, then proton diffuses from MoS<sub>2</sub> site to Ag site, and eventually forming H<sub>2</sub> and releases from MoS<sub>2</sub>-Ag boundary and Ag site. Our proof-of-concept study of unique molybdenum disulfide supported noble metal structure is expected to be a general strategy to improve the catalytic activity and stability of TMDCs.

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